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Pertraction of neodymium

M. Toure, G. Borda, D. Ode, J. Duhamet, S Pellet-Rostaing

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PERTRACTION OF NEODYMIUM



^{1,2}TOURE Moussa / ¹G. BORDA ; ¹D. ODE ; ¹J. DUHAMET ; ²S. P-ROSTAING

¹ CEA, DEN, DTEC, SGCS, F-30207 Bagnols-sur-Cèze, France

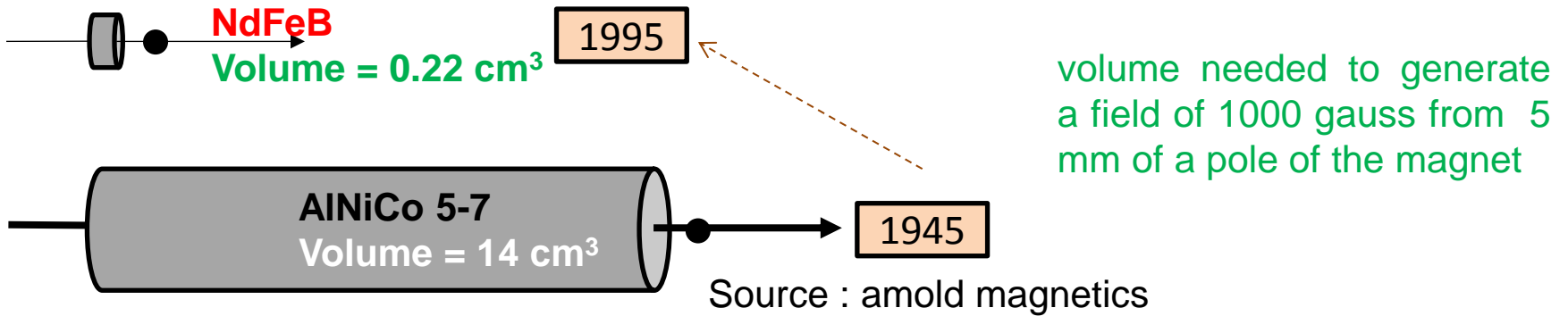
² ICSM, UMR5257, LTSM, F-30207 Bagnols-sur-Cèze

Presence of rare earth elements (REE) in permanent magnets

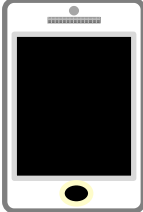
Elements	Nd	Dy	Pr
%	23-25	3.5-5	0.05-5

Others : Gd ; Tb

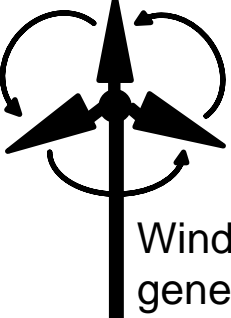
Prakash and al. ERES2014



Phones



Loud speakers
Microphones



Wind turbines
generators

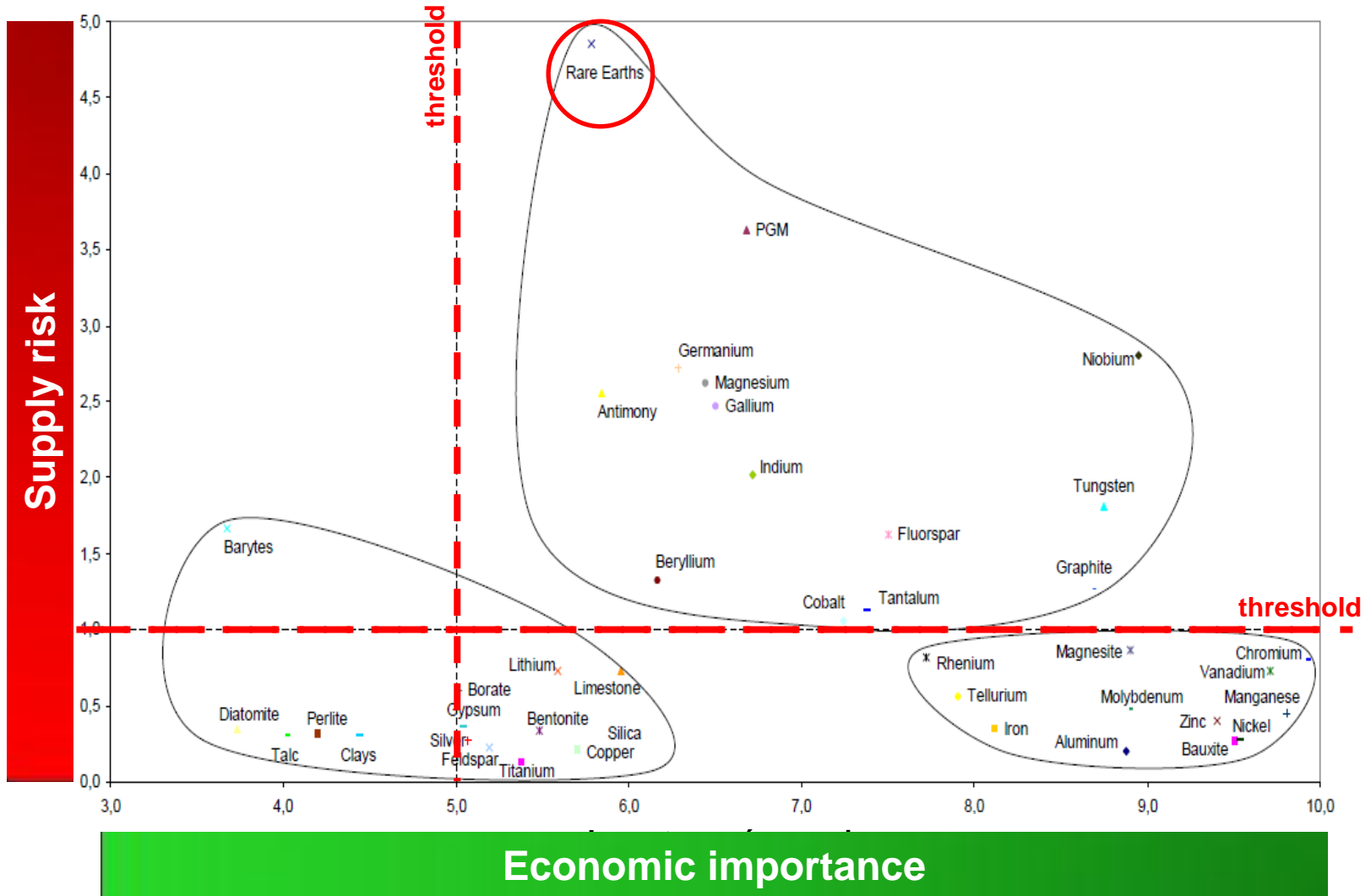
Some applications of permanent magnets (NdFeB)



The demand for Nd will rise by 700% over the next 25 years.

Why rare earth's recycling ?

Source : Report on Critical Raw Materials for the EU (May 2014)



 **Targets** : Ores and Waste Electrical and Electronic Equipment (WEEE)

Why rare earth's recycling ?

Global potential of REE recycling from magnets

REE application	Estimated REE stocks in 2020 (tons)	Estimated average lifetime (years)	Estimated REE old scrap in 2020 (tons)
Magnets	300,000.00	15	20,000.00

Koen and al. JOCP 51(2013) 1-22



Supply security ; no thorium issues.

Solvent extraction (SX) for rare earth recycling

Advantages of solvent extraction

- ⇒ Separation of compounds :
with similar properties (REE ; Ta-Nb),
- ⇒ High purity of final products :
REE (for optical and electronic products).

Others processes after leaching

- ⇒ Selective precipitation/electrodeposition,
- ⇒ Separation by ion exchange.

Some of SX process equipments : Pulsed column ; Centrifugal extractors
Mixer settlers : principle

Transfer of interest solute from aqueous phase to the solvent by mixing and settling of two phases.

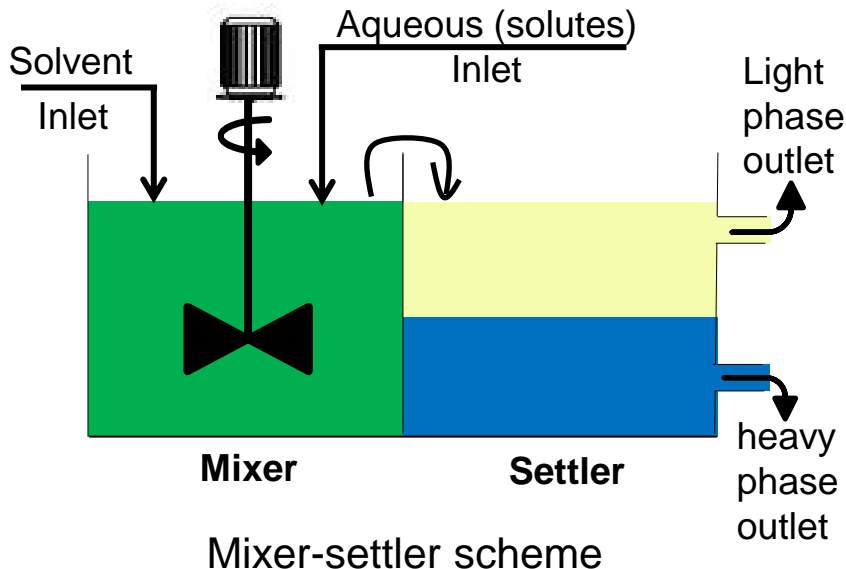
Drawbacks related with conventional equipments :

Impossible to use very emulsive solvents :
⇒ which extends the time of settling,

Density difference required for phases separation :
⇒ Using of diluent which can cause :

- ↳ third phase formation (avoid by adding a modifier in some cases) ;
- ↳ and a large volume of solvent in the process

Pertraction avoids the settling step and offers the possibility to operate without diluent



Contents

Pertraction : principle - interface stabilisation – advantages/drawbacks

Solvent L for neodymium's extraction : selection criteria

Neodymium's extraction : mechanism

Neodymium's extraction : temperature effect

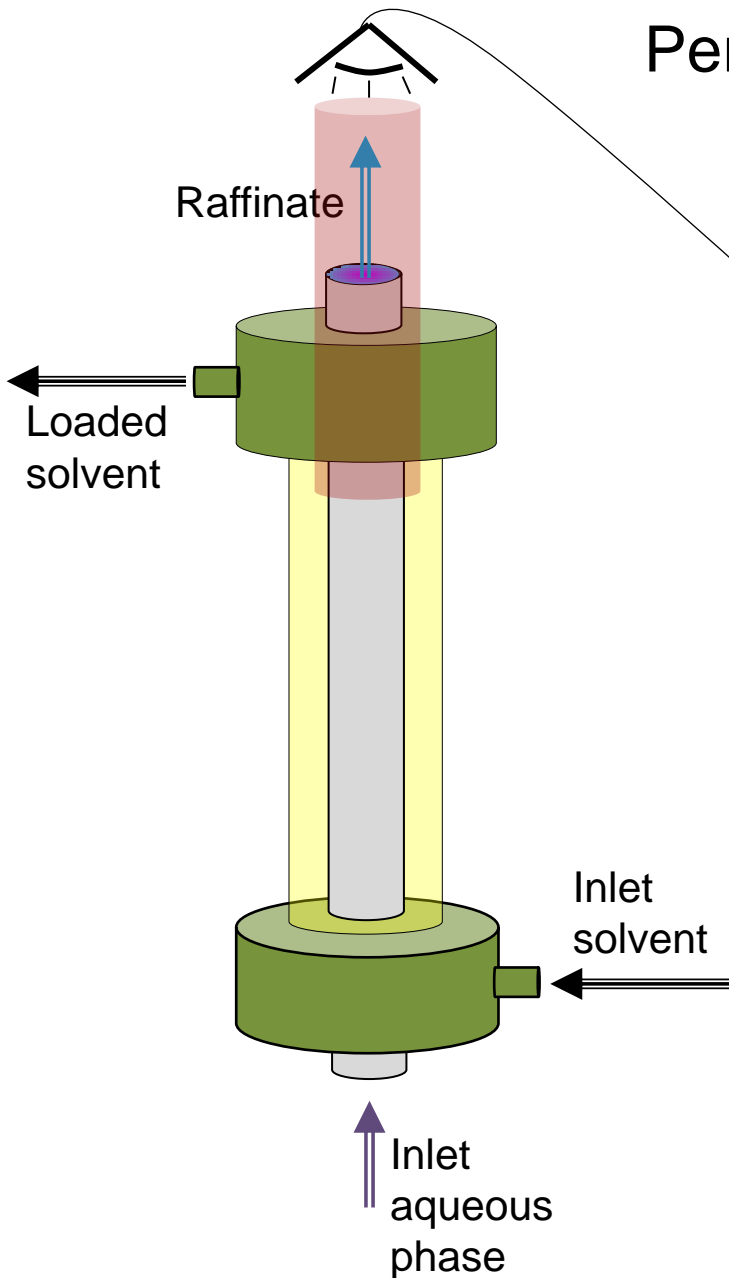
Recycle of REE : from magnets

Taylor Dispersion Analysis (TDA) : for neodymium's diffusion coefficient determination in aqueous and solvent L phases

Neodymium's extraction by pertraction : experiments and mass transfer simulation

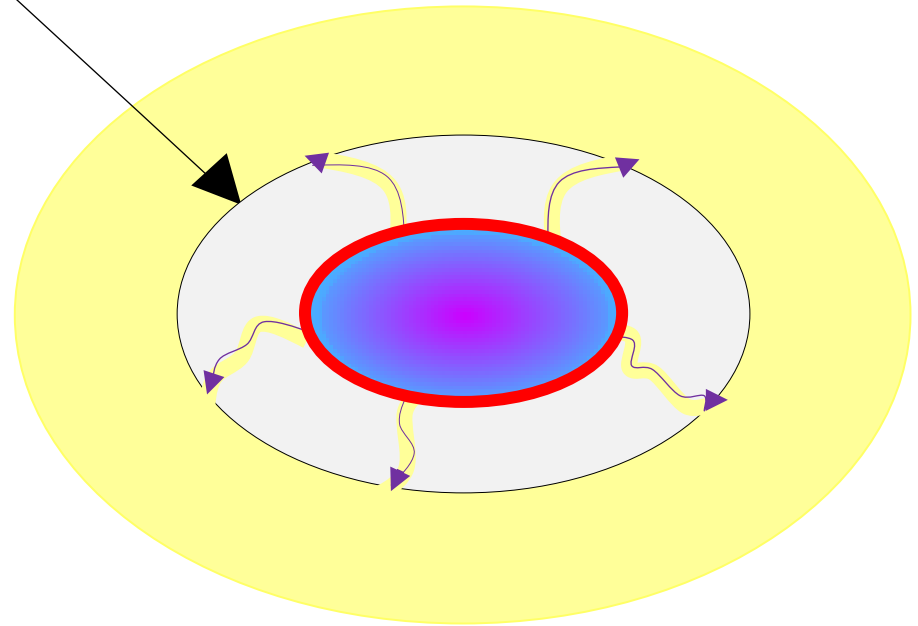
General conclusion

Pertraction : principle



solvent wets the hydrophobic membrane pores

Interface solvent – aqueous phase takes place at the pore mouth of the membrane



Mass transfer is governed by :
solute diffusion

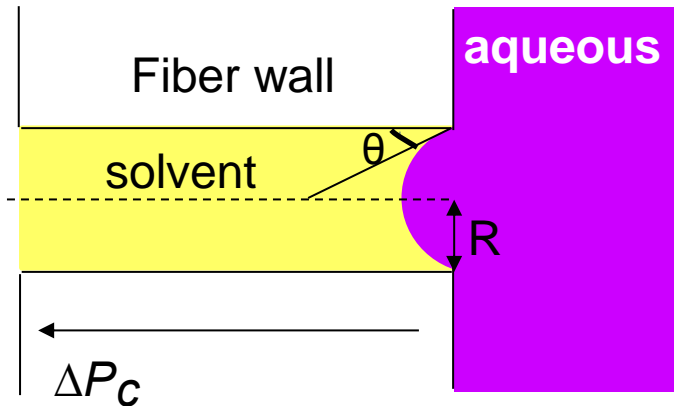
ΔC as driving force

Pertraction : solvent – aqueous interface stabilisation

Critical pressure

For maintain interface imobilized at pore mouth of the membrane :

$$(P_{aq} - P_{org}) < \Delta P_c$$



At $\Delta P \geq \Delta P_c$

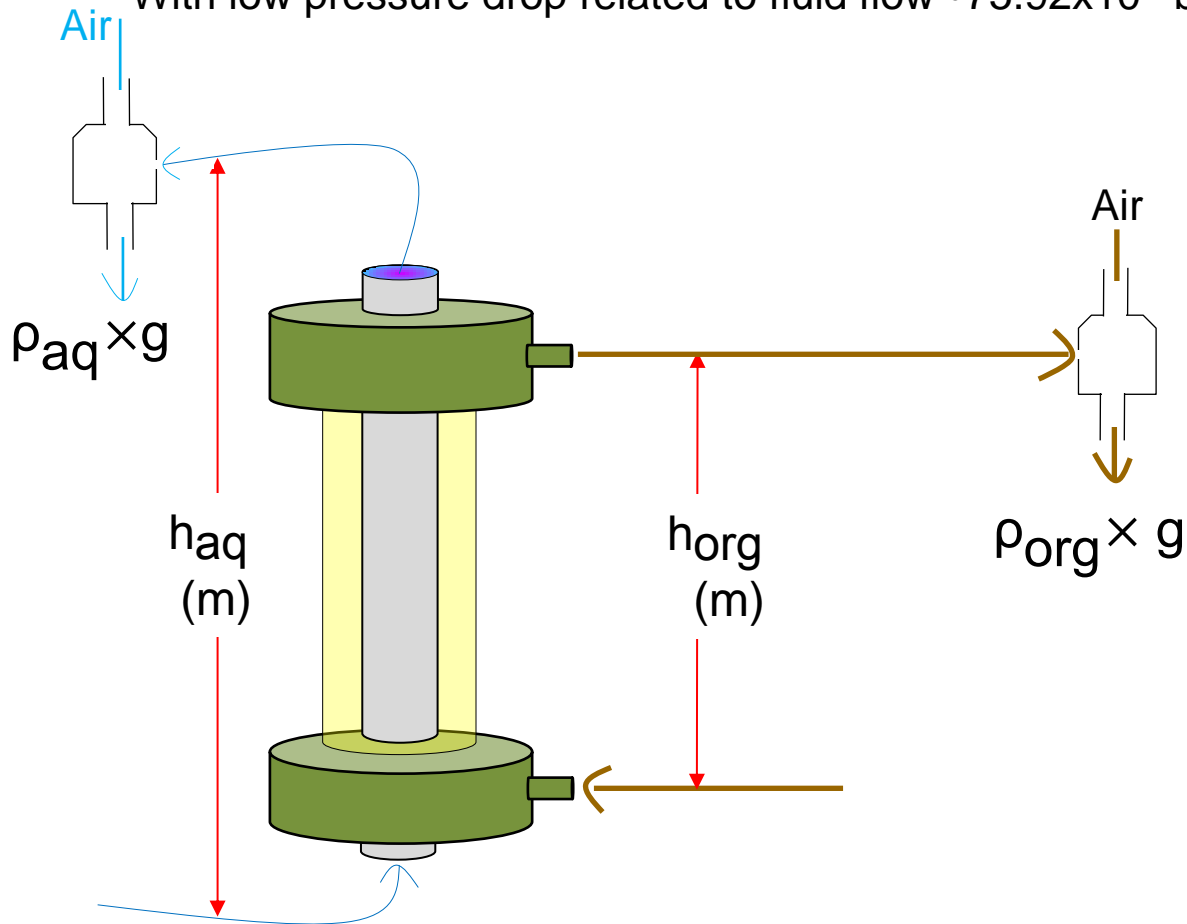
$$\Delta P_c = (P_{aq} - P_{org}) = \frac{2\sigma \cdot \cos \theta}{R}$$

σ interfacial tension ; θ wetting angle ; R pores radius

Pertraction : solvent – aqueous interface stabilisation

By hydrostatic pressure

With low pressure drop related to fluid flow $\sim 75.92 \times 10^{-5}$ bar

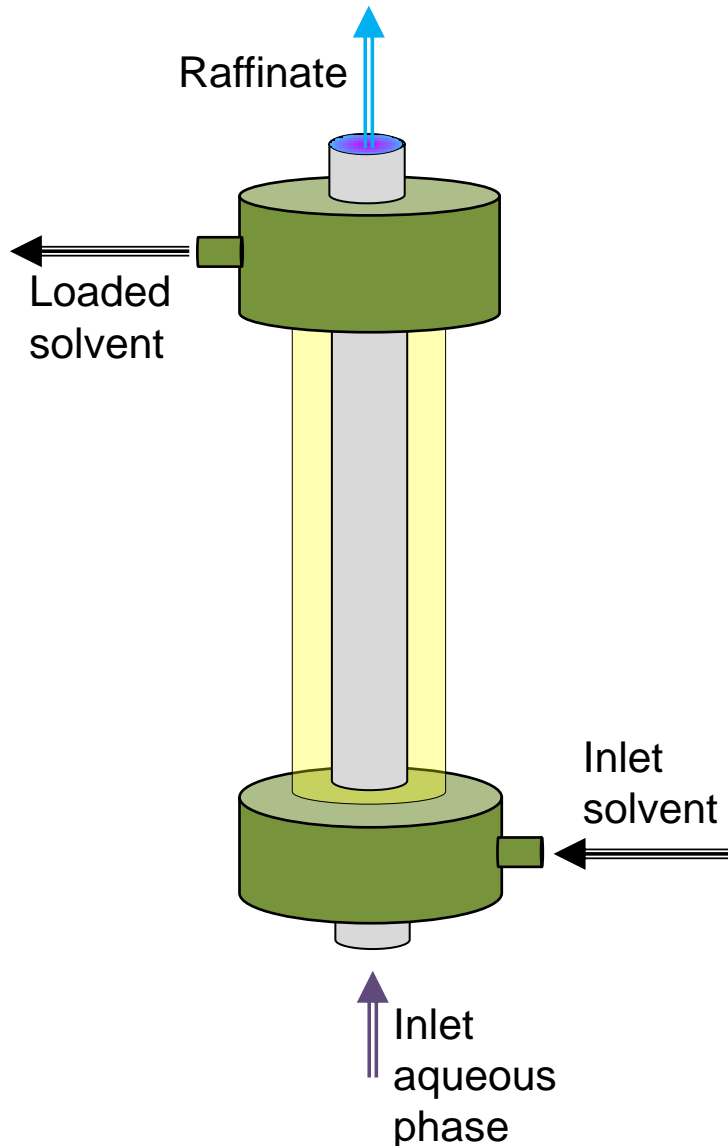


$$P_i = \rho_i \times g \times h_i$$

$i = aq \text{ or } org$

$$\Delta P = (P_{aq} - P_{org})$$

Pertraction : advantages / drawbacks



advantages

Possibility to use incompatible phases systems with conventional equipments :

- ⇒ Using very emulsive solvents
- ⇒ Operating without diluent
- ⇒ No density difference is required

Settling step is avoid

Simple implementation

Scale up without major difficulty

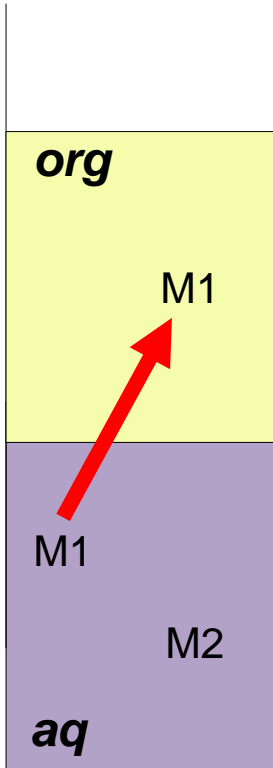
Drawbacks

Reduction of mass transfer related to the presence of the membrane

Fouling problems of the membrane

Solvent for neodymium's extraction : selection criteria

Selectivity



Distribution coefficient (K_D)

$$K_D = \frac{[C]_M^{\text{org}}}{[C]_M^{\text{aq}}}$$

Separation Factor ($SF_{M1/M2}$)

$$SF_{M1/M2} = \frac{K_D(M1)}{K_D(M2)}$$

Back-extraction ; solvent : solubility, flash point and cost.

Viscosity

As low as possible for minimize pressure drop and enhance mass transfer at aqueous and organic interface :

Fick's first law

$$J = -D \nabla c$$

Stokes-Einstein

$$D = \frac{k_B T}{R_h 6\pi\eta}$$

Conditions :

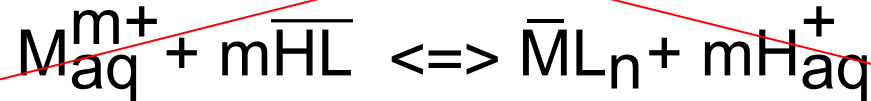
Batch process at $T(^{\circ}\text{C})$,
Time, O/A

k_B : Boltzmann constant η : viscosity of solvent
 R_h : hydrodynamic radius of solvent complexes

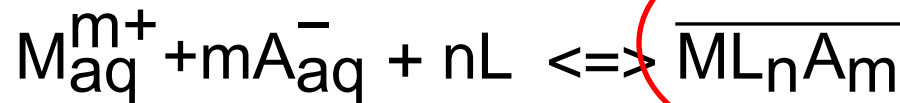
Neodymium's extraction : mechanism

The main mechanisms for neodymium extraction

~~By ion exchange~~



 By solvation



Mass
spectroscopy

Slope
Analysis K_D

Marcus and al. have described the four mechanisms in solvent extraction :
« *Ion Exchange and Solvent Extraction of Metal Complexes, Wiley-Interscience, 1969* »

Neodymium's extraction : mechanism



Law of mass action

$$K_{\text{ex}}^{\text{app}} = \frac{[\overline{\text{NdL}_n(\text{NO}_3)_3}]}{[\text{Nd}^{3+}] \cdot [\text{NO}_3]_3 \cdot [\text{L}]_{\text{free}}^n} = \frac{K_D}{[\text{NO}_3]_3 \cdot [\text{L}]_{\text{free}}^n}$$

Slope analysis technique

$$\log K_D = n \cdot \log [\text{L}]_{\text{free}} + 3 \cdot \log [\text{NO}_3] + \log K_{\text{ex}}^{\text{app}}$$

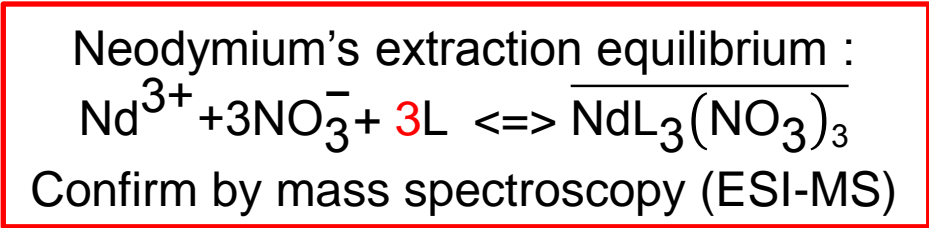
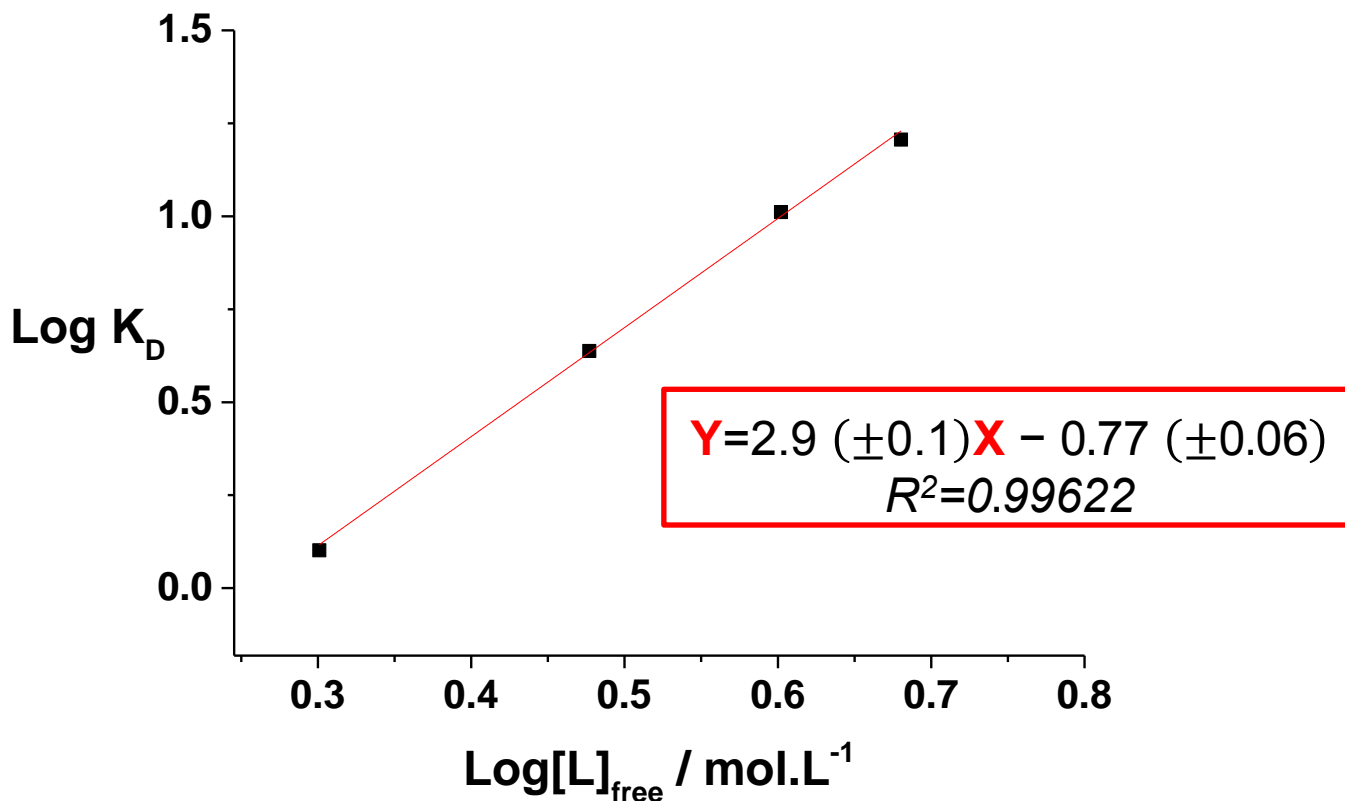
$y = A \cdot x + B$

Experimental conditions

$$[\text{HNO}_3] = 0.1 \text{ M} ; [\text{NaNO}_3] = 2.5 \text{ M} ; [\text{Nd}] = 6 \cdot 10^{-3} \text{ M} ; A/O = 1 ; T = 20-22^\circ\text{C}$$

$$\text{Log}(K_D) = f(\text{Log}[L]_{\text{free}})$$

Neodymium's extraction : mechanism



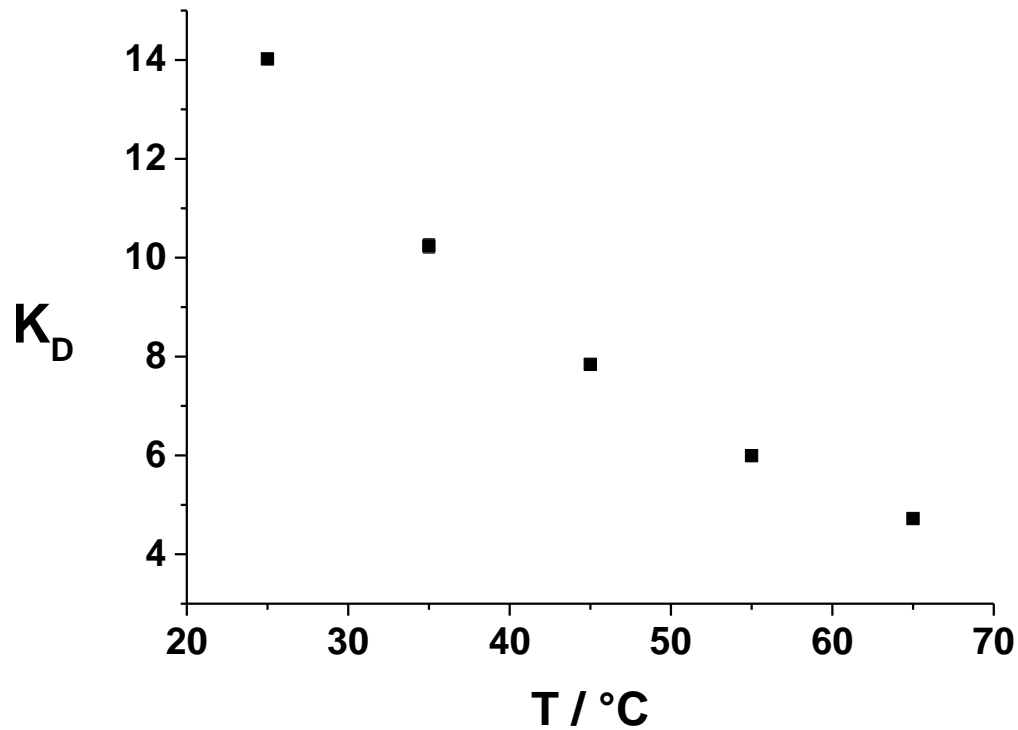
ESI-MS : Mass Spectroscopy by Electrospray Ionization

Neodymium's extraction : temperature effect

Experimental conditions

$[\text{HNO}_3] = 0.1 \text{ M}$; $[\text{NaNO}_3] = 2.5 \text{ M}$; $[\text{Nd}] = 6 \cdot 10^{-3} \text{ M}$; $A/O = 1$

$$K_D = f(T^\circ\text{C})$$



☞ Exothermique extraction with $K_D \in [14 - 5]$

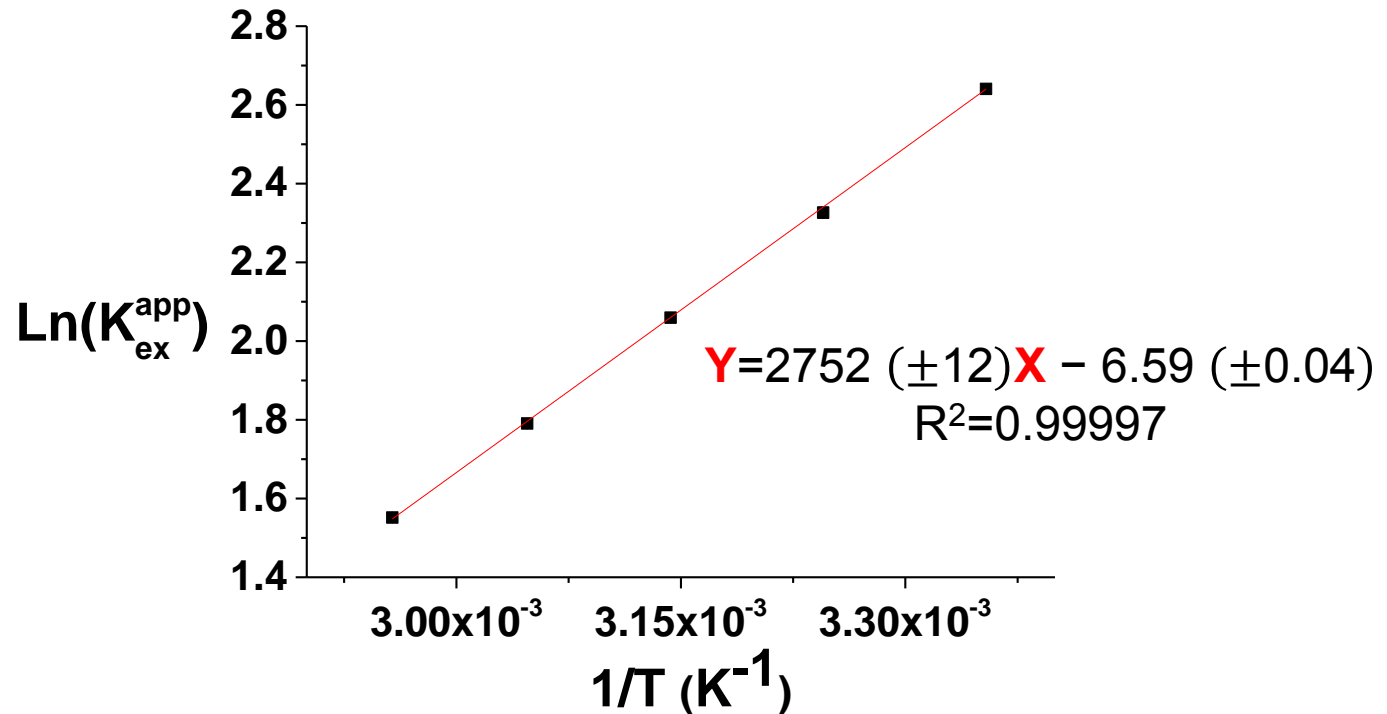
Neodymium's extraction : temperature effect

Law of mass action

$$K_{\text{ex}}^{\text{app}} = \frac{K_{\text{D}}}{[\text{NO}_3]_3 \cdot [\text{L}]^3}$$

Van't Hoff equation

$$\ln K_{\text{ex}}^{\text{app}} = \frac{-\Delta H_{\text{ext}}^0}{R} \times \frac{1}{T} + \frac{\Delta S_{\text{ext}}^0}{R} + 3\ln[\text{NO}_3] + 3\ln[\text{L}]$$



$$\Delta H_{\text{ext}}^0 = -22.9 \text{ kJ.mol}^{-1}$$

Recycle of REE

Experimental conditions

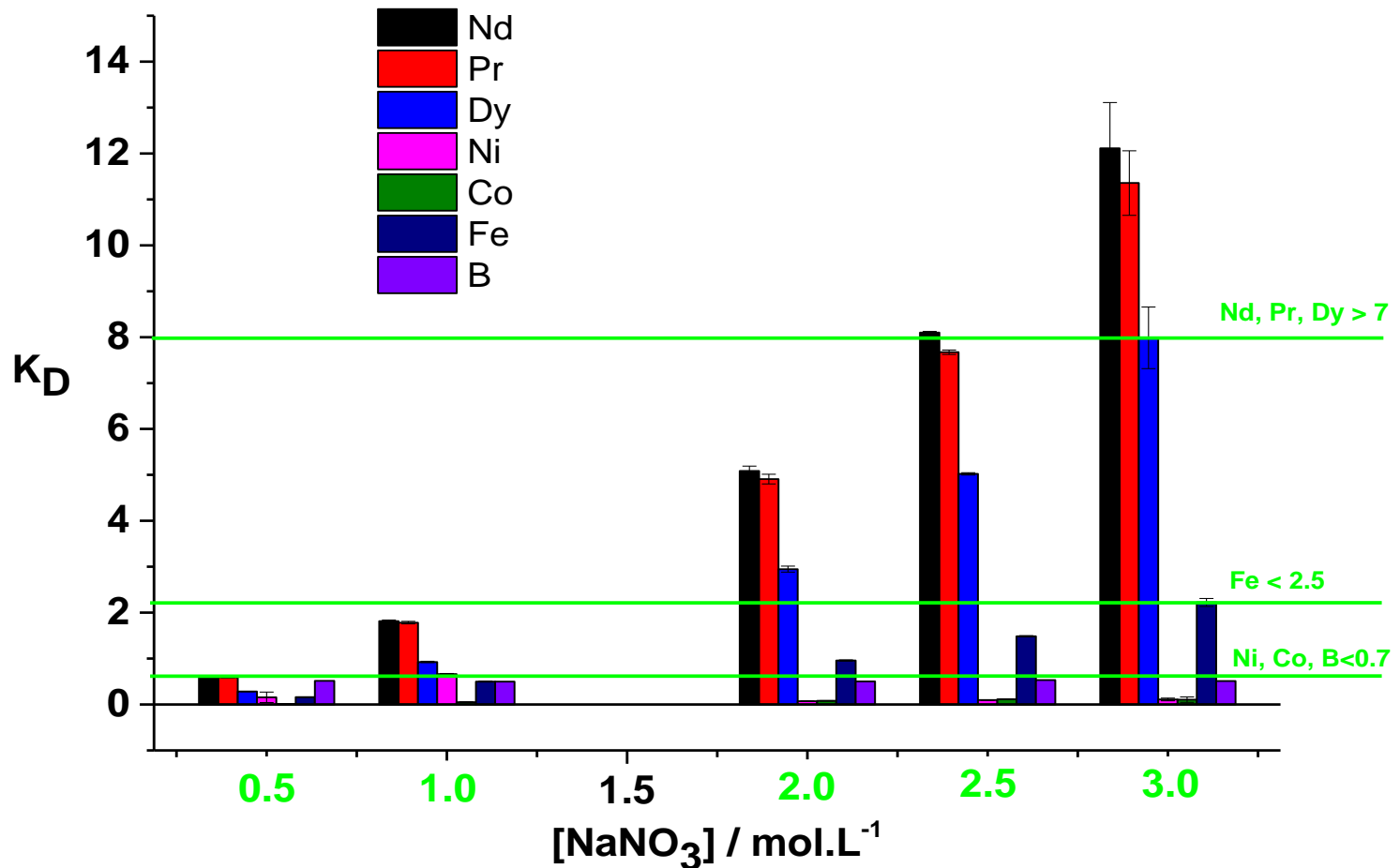
$[\text{HNO}_3] = 0.1 \text{ M}$; $[\text{NaNO}_3] = [0.5 - 3] \text{ M}$; $A/O=1$

Elements /g.L⁻¹						
Nd	Pr	Dy	B	Fe	Ni	Co
0.3	0.3	0.3	0.2	0.3	0.3	0.3

waste model of magnets

Recycle of REE

Distribution coefficients *versus* $[\text{NaNO}_3]$



NO_3^- favors extraction of Nd, Pr, Dy and Fe
Solvent L extracts significantly Nd, Pr, Dy with $K_D \in [7 - 12]$
Fe is the main impurity with $K_D < 2.5$

Recycle of REE

Separation factors *versus* $[\text{NaNO}_3]$

$[\text{NaNO}_3] / \text{mol.L}^{-1}$	3
SF Nd/Fe	5.44
SF Nd/Ni	116.037
SF Nd/Co	154.03
SF Nd/B	30

$[\text{NaNO}_3] / \text{mol.L}^{-1}$	0.5
SF Nd/Pr	1.039
SF Nd/Dy	2.17
SF Pr/Dy	2.088



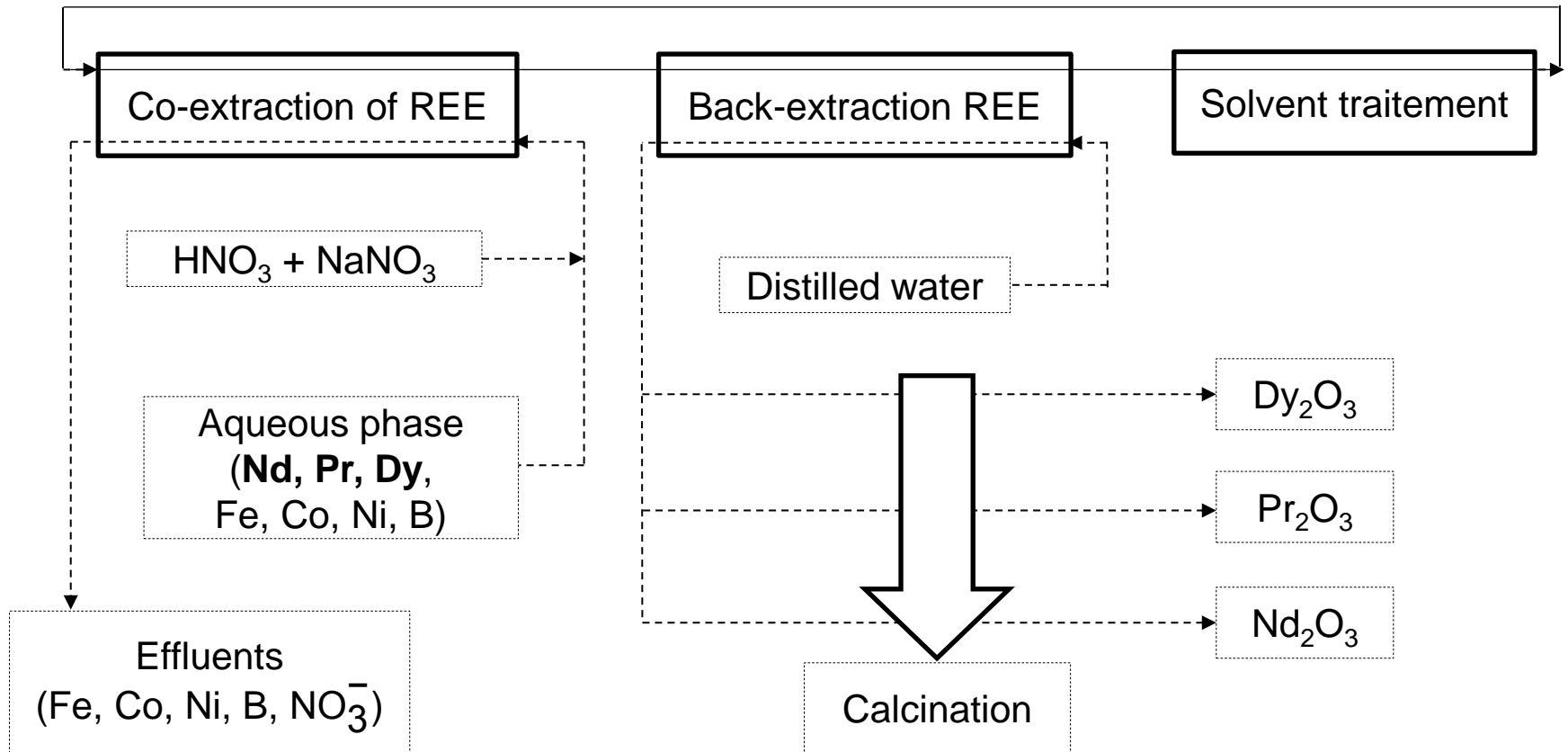
Selective extraction of REE at NaNO_3 (3M) and possibility to separate them each other at NaNO_3 (0.5M)



REE back-extraction can be made at low acidity.

Recycle of REE

Scheme of process



 Liquid-liquid extraction equipment with required stages

Taylor Dispersion Analysis (TDA) : for neodymium's diffusion coefficient determination in aqueous and solvent L phases

solvent L name is not mentioned here for confidential aspect

^{1,2}TOURE Moussa / ¹G. BORDA ; ¹D. ODE ; ¹J. DUHAMET ; ²S. P-ROSTAING

Collaboration with ³J. CHAMIEH ; ³H. COTTET

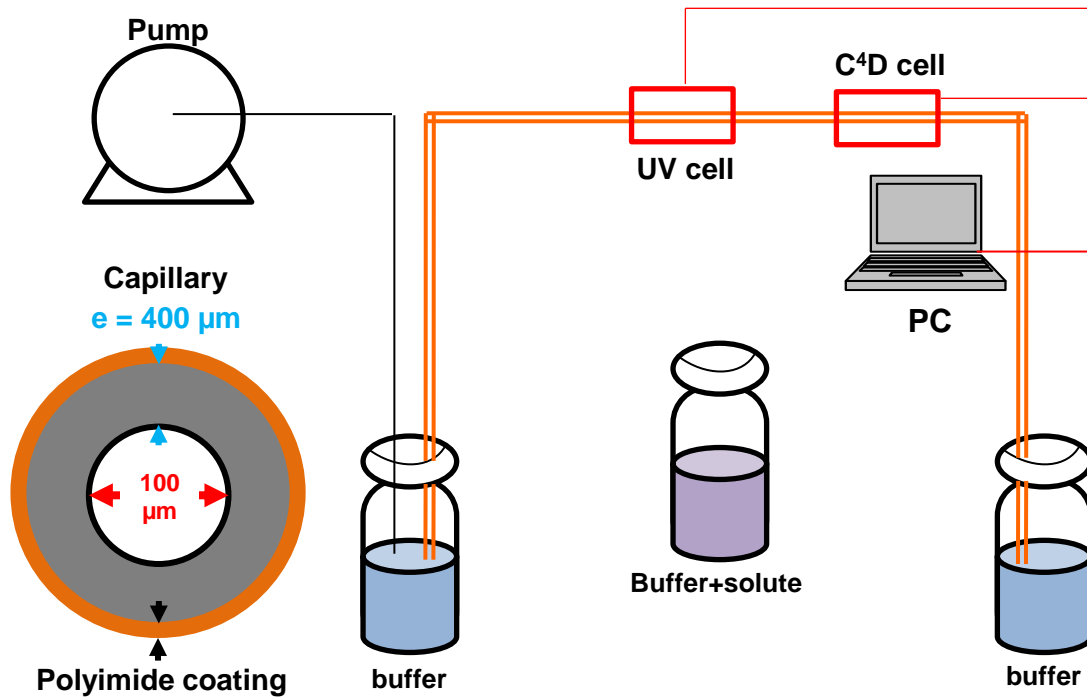
¹ CEA, DEN, DTEC, SGCS, F-30207 Bagnols-sur-Cèze, France

² ICSM, UMR5257, LTSM, F-30207 Bagnols-sur-Cèze

³ IBMM, UMR 5247-UM2, DSBC, place Eugène Bataillon CC 017, 34095 Montpellier Cedex 5, France

Taylor Dispersion Analysis (TDA)

Capillary electrophoresis (CE) for TDA



Theory

Taylor – Aris –Golay equation

$$H = \frac{2D}{u} + \frac{R_C^2}{24D} \quad H = \frac{l_D \sigma^2}{t_R^2}$$

(Note: In the original image, the first term is crossed out and labeled 'Axial diffusion', and the second term is labeled 'Taylor Dispersion')

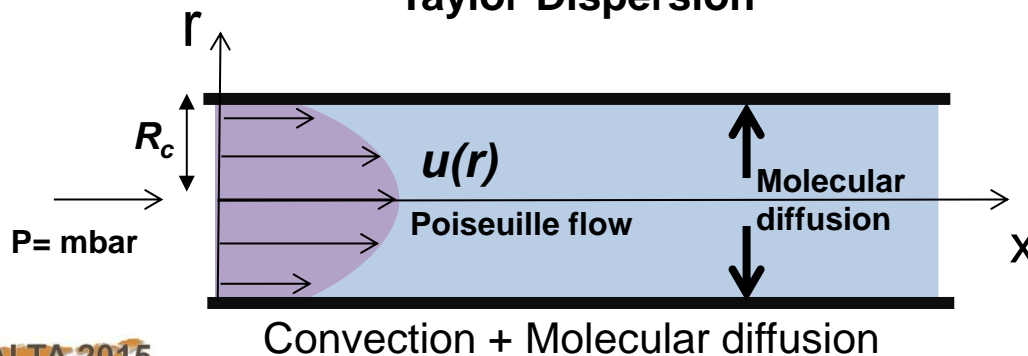
Axial diffusion

- H : Plate height
 σ^2 : Variance of the elution profile
 u : linear velocity
 t_D : average elution time
 l_D : capillary Length to the detector
 R_C : capillary radius

Reduced to :

$$D = \frac{R_C^2}{24\sigma^2} t_R$$

Taylor Dispersion



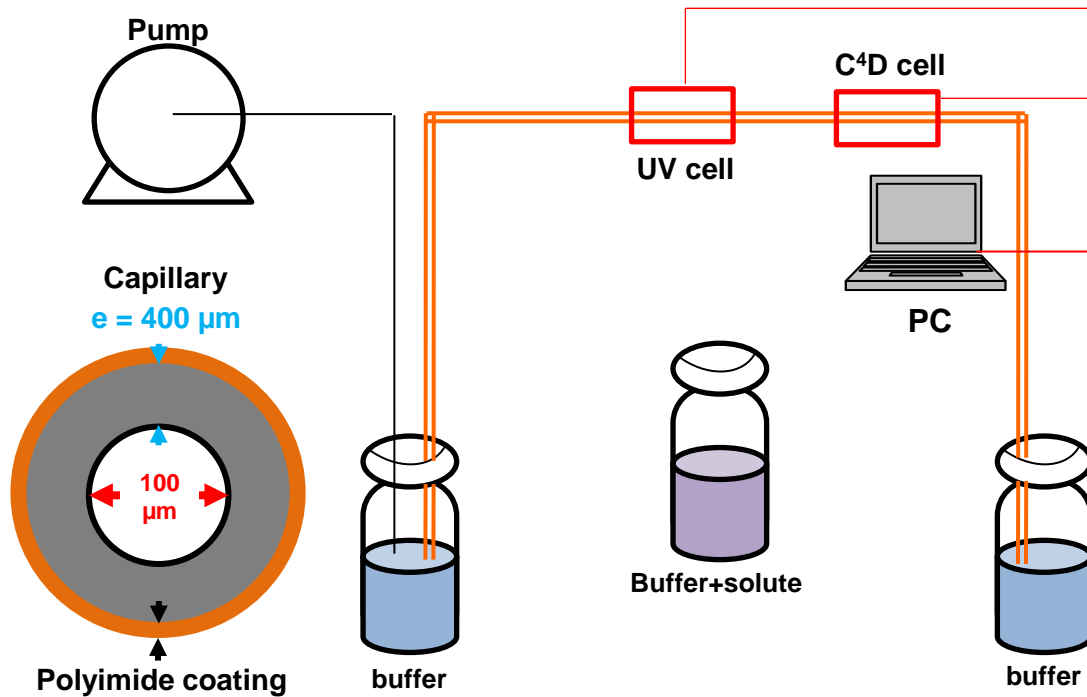
Validity :

$$\text{Satisfied if : } \tau = \frac{Dt_R}{R_C^2} \geq 1.25$$

$$\text{Satisfied if : } Pe = \frac{R_C u}{D} \geq 40$$

Taylor Dispersion Analysis (TDA)

Capillary electrophoresis (CE) for TDA



Theory

Taylor – Aris –Golay equation

$$H = \frac{2D}{u} + \frac{R_C^2}{24D} \quad H = \frac{l_D \sigma^2}{t_R^2}$$

(Note: In the original image, the terms $\frac{2D}{u}$ and $\frac{R_C^2}{24D}$ are crossed out and labeled as Axial diffusion and Taylor Dispersion respectively.)

H : Plate height
 σ^2 : Variance of the elution profile
u : linear velocity
 t_D : average elution time
 l_D : capillary Length to the detector
 R_C : capillary radius

Reduced to :

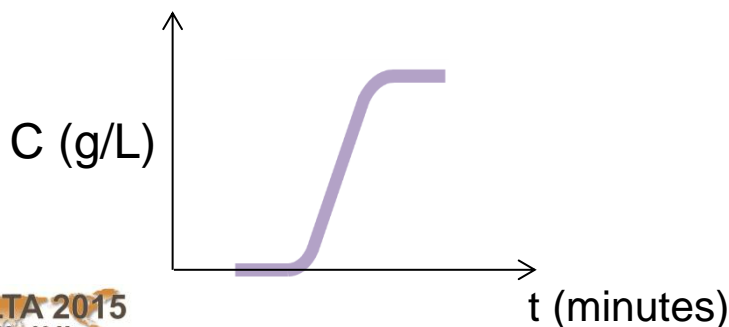
$$D = \frac{R_C^2}{24\sigma^2} t_R$$

Validity :

$$\text{Satisfied if : } \tau = \frac{Dt_R}{R_C^2} \geq 1.25$$

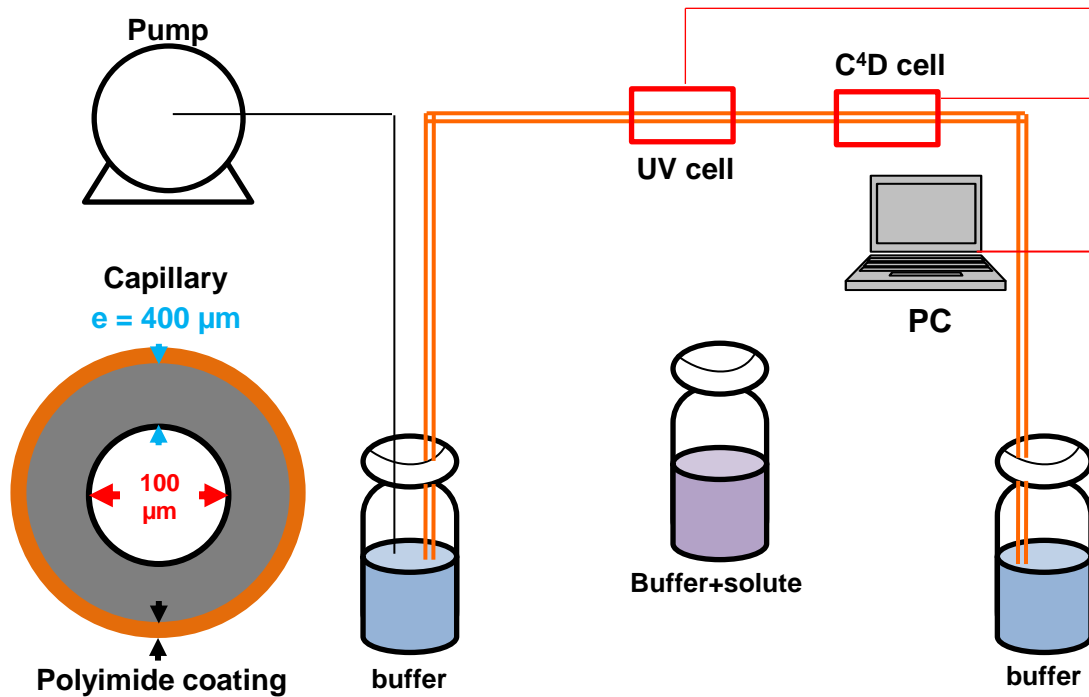
$$\text{Satisfied if : } Pe = \frac{R_C u}{D} \geq 40$$

Taylor Dispersion



Taylor Dispersion Analysis (TDA)

Capillary electrophoresis (CE) for TDA



Theory

Taylor – Aris –Golay equation

$$H = \frac{2D}{u} + \frac{R_C^2}{24D} \quad H = \frac{l_D \sigma^2}{t_R^2}$$

(Note: In the original image, the first equation is partially crossed out with a blue line, and the second equation is highlighted in red.)

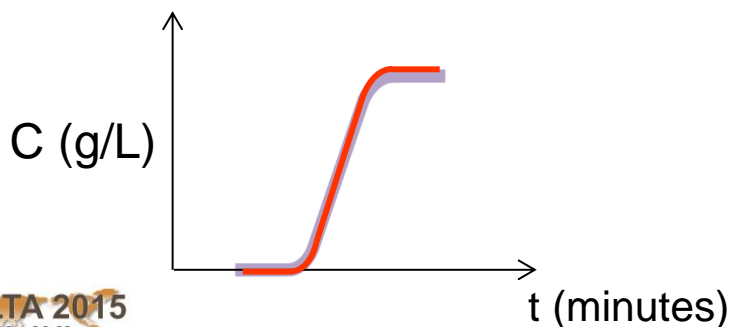
Axial diffusion

H : Plate height
 σ^2 : Variance of the elution profile
 u : linear velocity
 t_D : average elution time
 l_D : capillary Length to the detector
 R_C : capillary radius

Reduced to :

$$D = \frac{R_C^2}{24\sigma^2} t_R$$

Taylor Dispersion

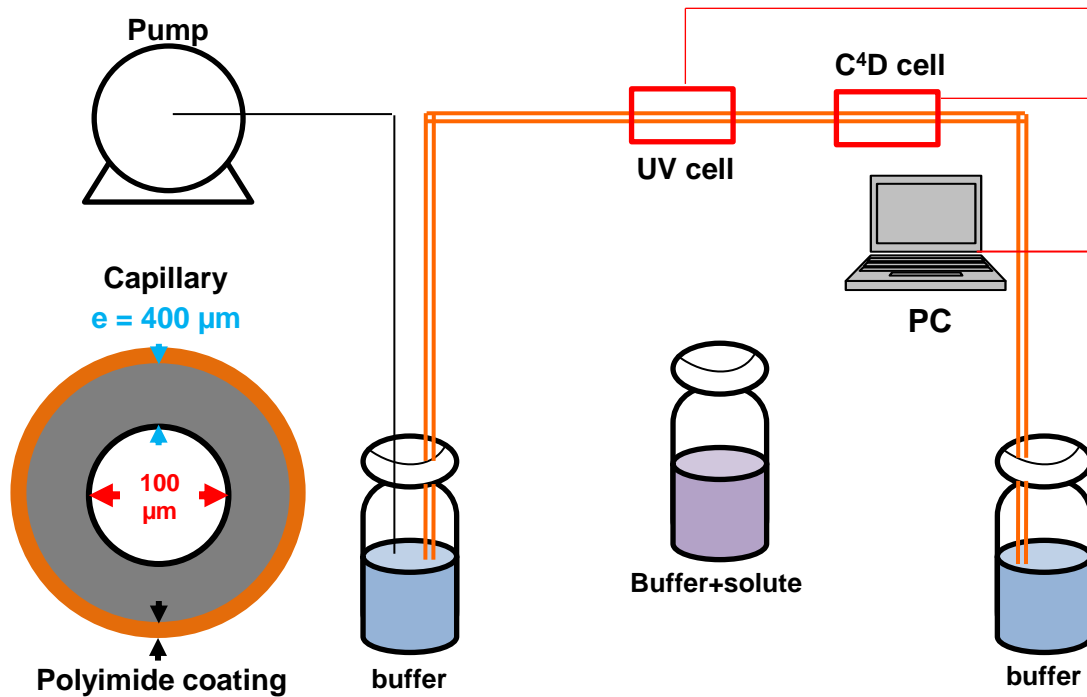


In practise, D is calculated by fitting the experimental profile with a Gauss error function for determine σ and t_R :

$$\frac{C}{C_0} = \frac{1}{2} \pm \frac{1}{2} \operatorname{erf} \left[\frac{(t - t_R)}{\sigma\sqrt{2}} \right]$$

Taylor Dispersion Analysis (TDA)

Capillary electrophoresis (CE) for TDA



Advantages of TDA

- Simple ;
- Fast ;
- Low sample volume (0,7 nL) ;

Theory

Taylor – Aris –Golay equation

$$H = \frac{2D}{u} + \frac{R_C^2}{24D} \quad H = \frac{l_D \sigma^2}{t_R^2}$$

(Note: In the original image, the first equation is color-coded: 2D is blue, u is blue, R_C^2 is red, and 24D is red. The second equation is black.)

Axial diffusion

- H : Plate height
- σ^2 : Variance of the elution profile
- u : linear velocity
- t_D : average elution time
- l_D : capillary Length to the detector
- R_C : capillary radius

Reduced to :

$$D = \frac{R_C^2}{24\sigma^2} t_R$$

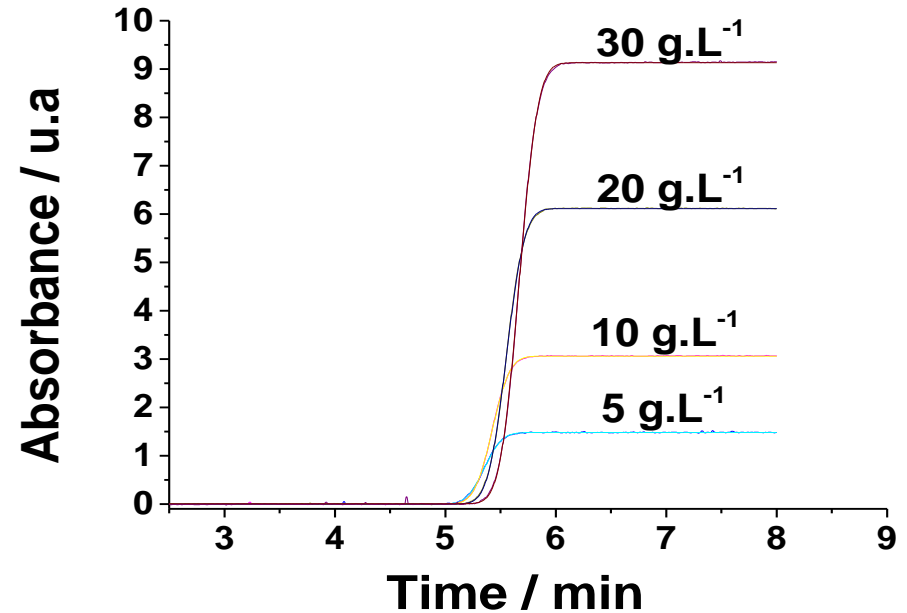
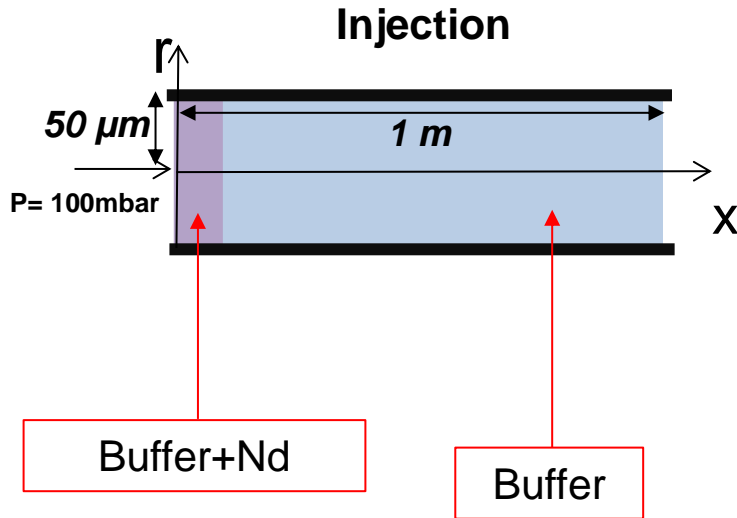
Validity :

$$\text{Satisfied if : } \tau = \frac{Dt_R}{R_C^2} \geq 1.25$$

$$\text{Satisfied if : } Pe = \frac{R_C u}{D} \geq 40$$

Taylor Dispersion Analysis (TDA)

Neodymium's diffusion coefficient in aqueous phase



Validity

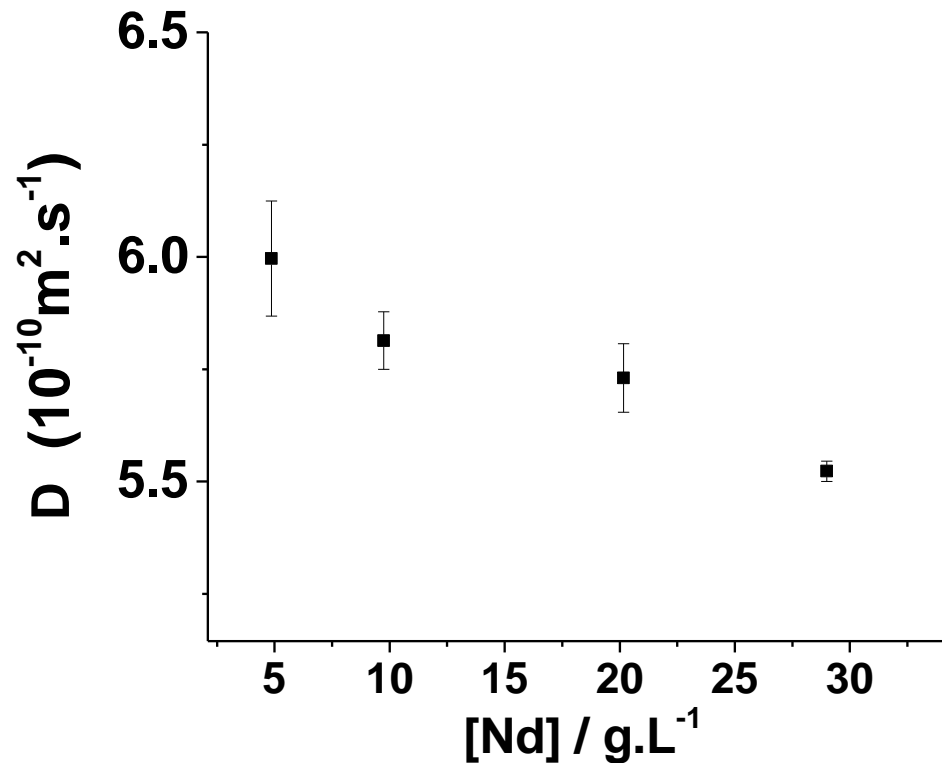
buffer

$$Pe \in [255 - 276] \geq 40$$

$$\tau \in [66.2 - 71.9] > 1.25$$

Taylor Dispersion Analysis (TDA)

Neodymium's diffusion coefficient in aqueous phase



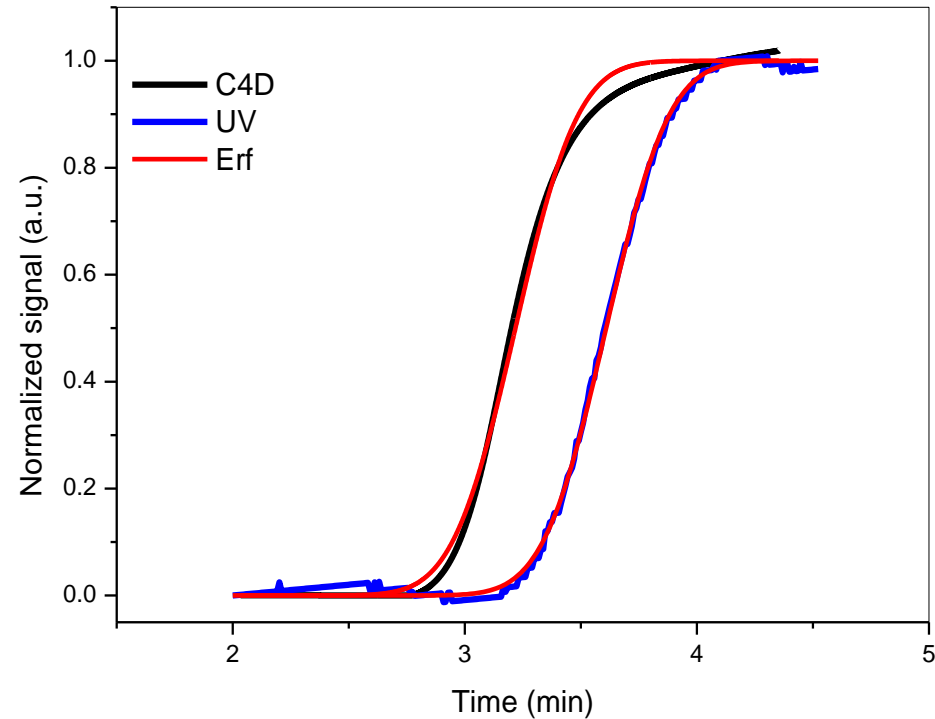
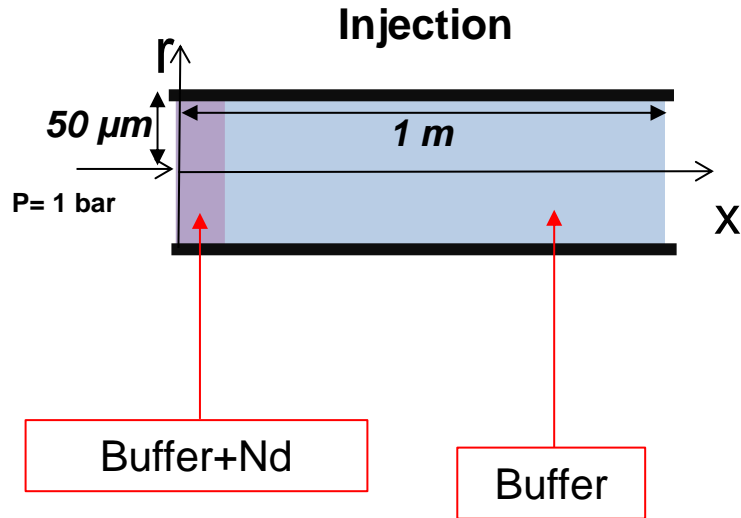
$$D_{\text{Nd}} \in [5.99 - 5.52] \cdot 10^{-10} \text{ m}^2 \cdot \text{s}^{-1}$$

with $RSD < 3 \%$

Same order of magnitude as the one calculated with Nernst–Einstein equation
 $D_0 = 6.16 \cdot 10^{-10} \text{ m}^2 \cdot \text{s}^{-1}$ (with conductivity of Nd $\sigma = 69.4 \mu\text{S} \cdot \text{cm}^{-1}$)

Taylor Dispersion Analysis (TDA)

Neodymium's diffusion coefficient in solvent L phase



Validity

$$Pe = 1910 \geq 40$$

$$\tau = 9.58 \geq 1.25$$

Taylor Dispersion Analysis (TDA)

Neodymium's diffusion coefficient in solvent L phase

at 1 g.L⁻¹ with UV-Vis and C⁴D detectors

D / 10⁻¹⁰ m².s⁻¹	
C⁴D	UV-Vis
1.33	1.41

with UV-Vis detector

[Nd] / g.L⁻¹	D / 10⁻¹⁰ m².s⁻¹
1	1.13
8	0.88
21	0.41

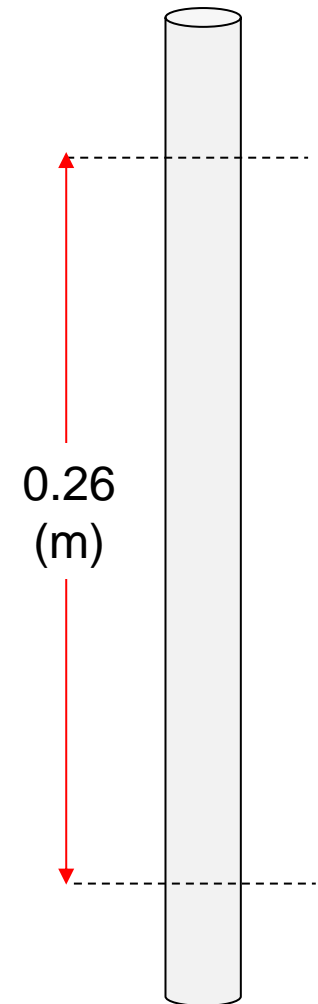
Neodymium's extraction by pertraction

with solvent L which name is not mentioned here for confidential aspect

Pertraction : experimental module

Hollow fiber : hydrophobic polypropylene membrane

property	value	unit
Length (L)	0.25	m
Internal radius (R_{int})	$0,9 \times 10^{-3}$	m
Thickness (e)	0.4×10^{-3}	m
Tortuosity (τ)	2	-
Volume	0.635×10^{-6}	m^3
Interfacial area	1.148×10^{-3}	m^2
Interfacial volumic area	230	$m^2.m^{-3}$
Porosity (ϵ)	80	%
Pore radius (R_p)	100	nm



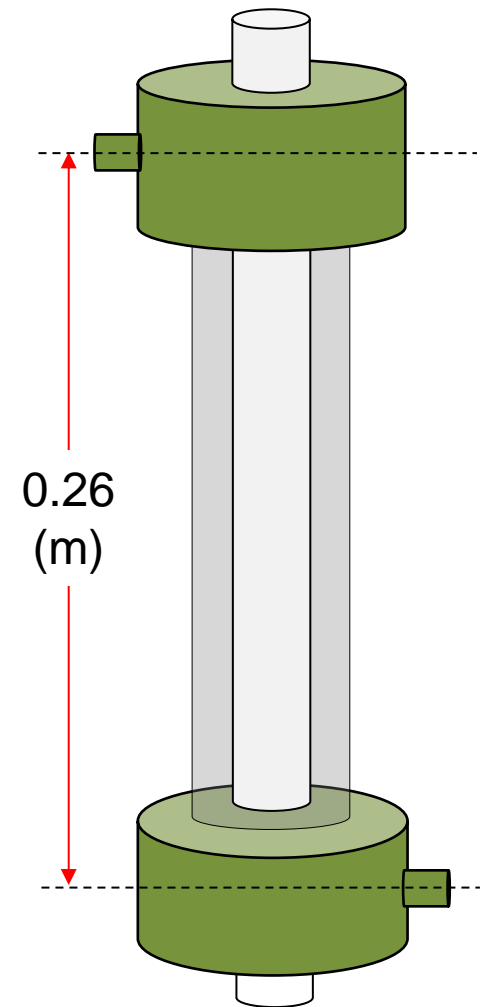
From Alting
(France)

Pertraction : experimental module

Glass potting around the fiber

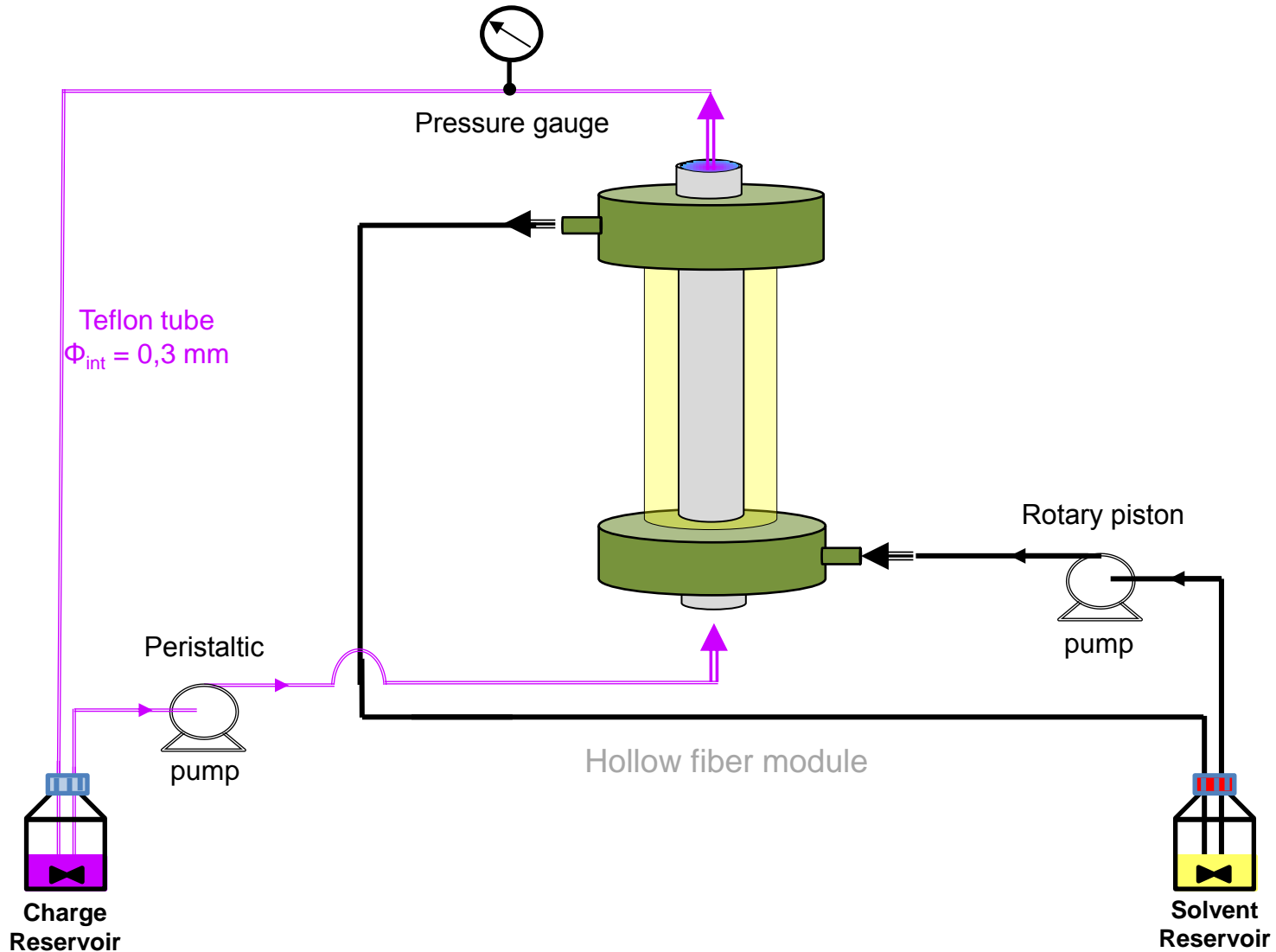
Property	Value	unit
Length (L_p)	0.26	m
Internal radius (R_{intp})	$2.5 \cdot 10^{-3}$	m
Volume	4.984×10^{-6}	m^3

Low interfaciale volumic area $230 \text{ m}^2 \cdot \text{m}^{-3}$



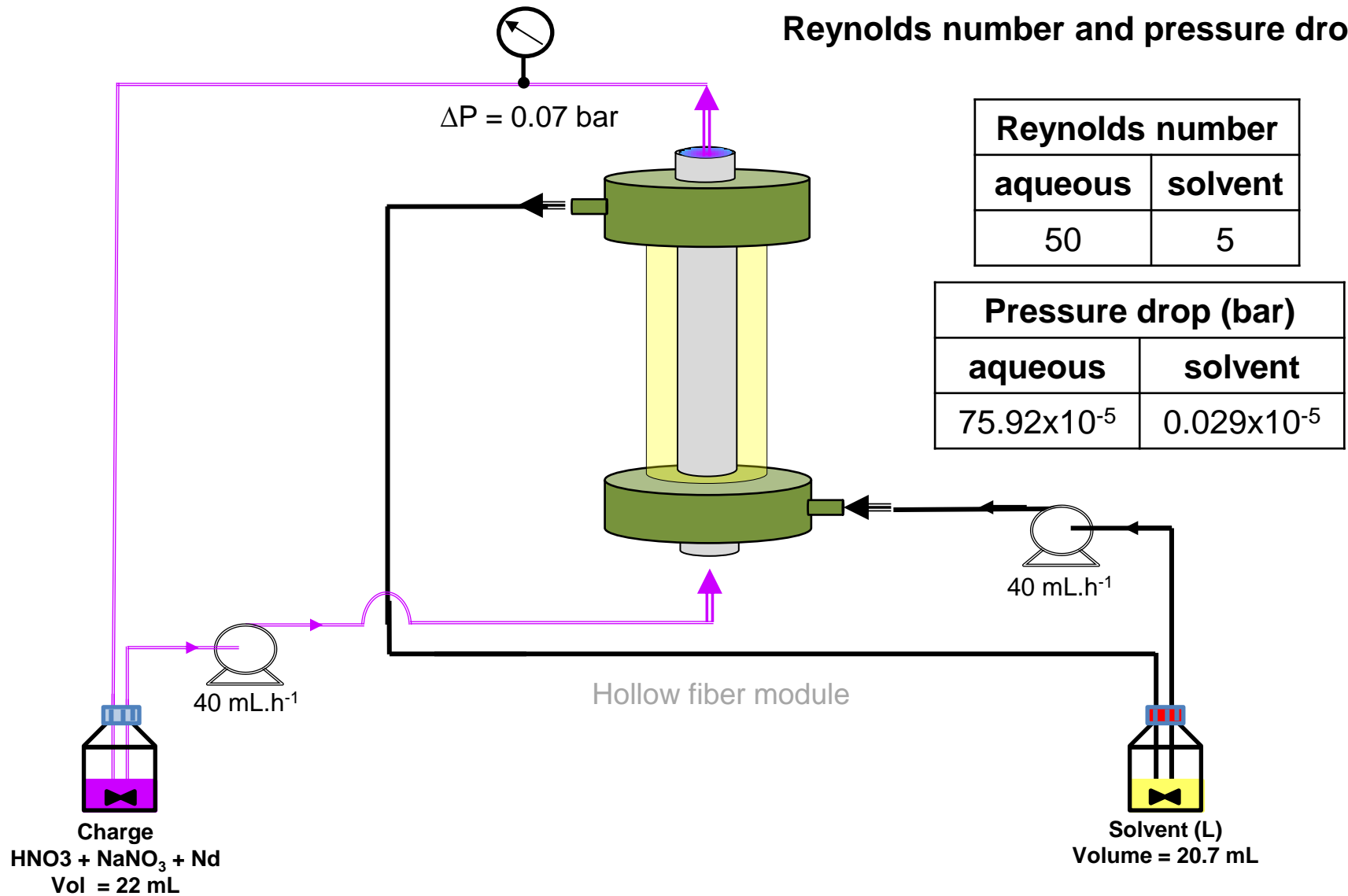
Pertraction : experimental set-up

Co-current contact – recycle mode

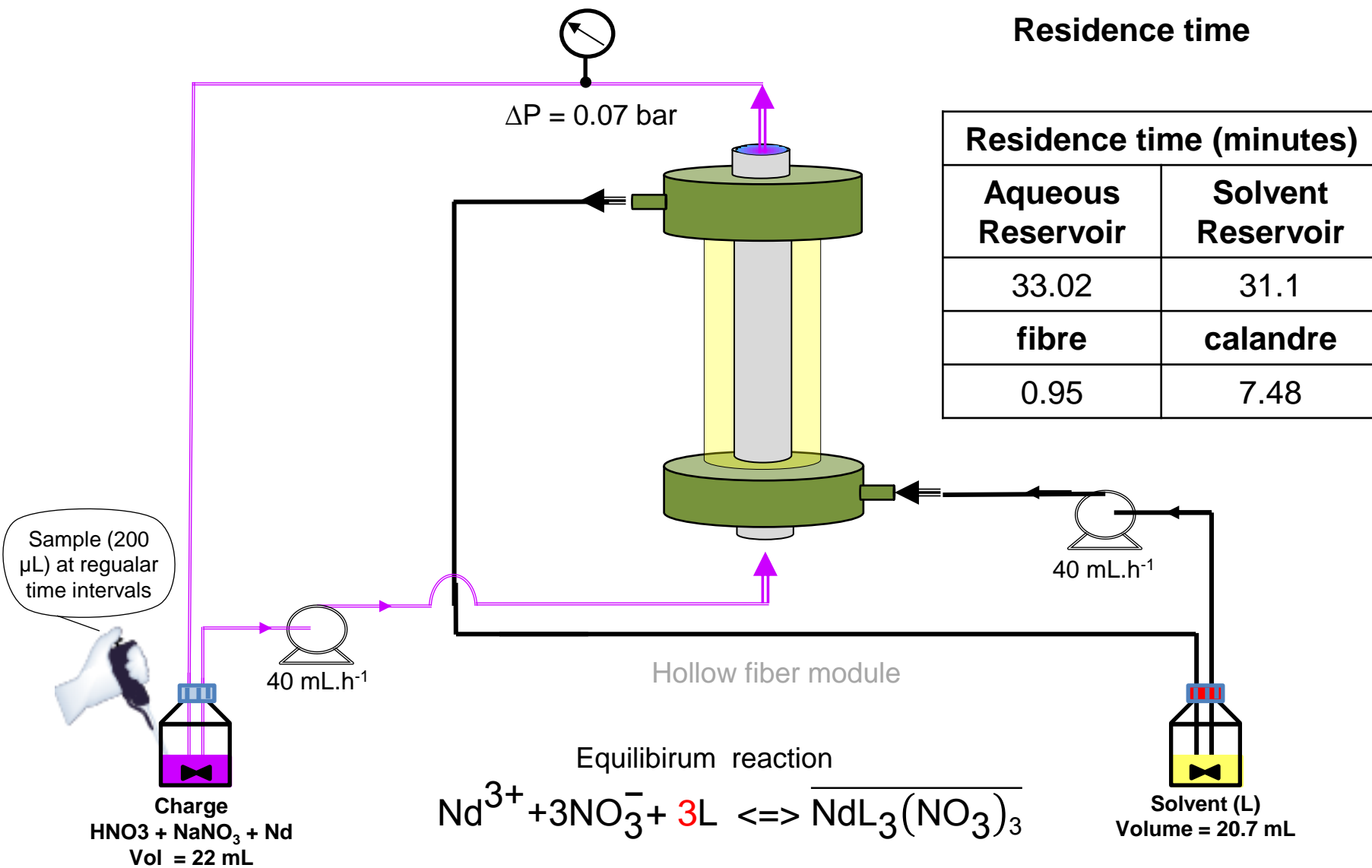


Pertraction : experimental conditions

Reynolds number and pressure drop



Pertraction : experimental conditions



Pertraction : experimental results

Aqueous samples are analysed by ICP-OES to estimate the concentration of Nd ions. Their concentration in solvent L phase is determined by mass balance describe below :

$$\underbrace{V_{aq} \cdot X_e + V_{org} \cdot Y_e^0}_{\text{Inlet}} = \underbrace{V_{org} \cdot Y_1 + V_{aq} \cdot X_1}_{\text{Outlet}}$$

$$V_{aq} \cdot X_e - \sum V_{pe} \cdot X_{n-1} = V_{org} \cdot Y_n + [V_{aq} - (n-1) \cdot V_{pe}] \cdot X_n$$

V: volume of phases (mL), org (solvent L) and aq (aqueous) ;

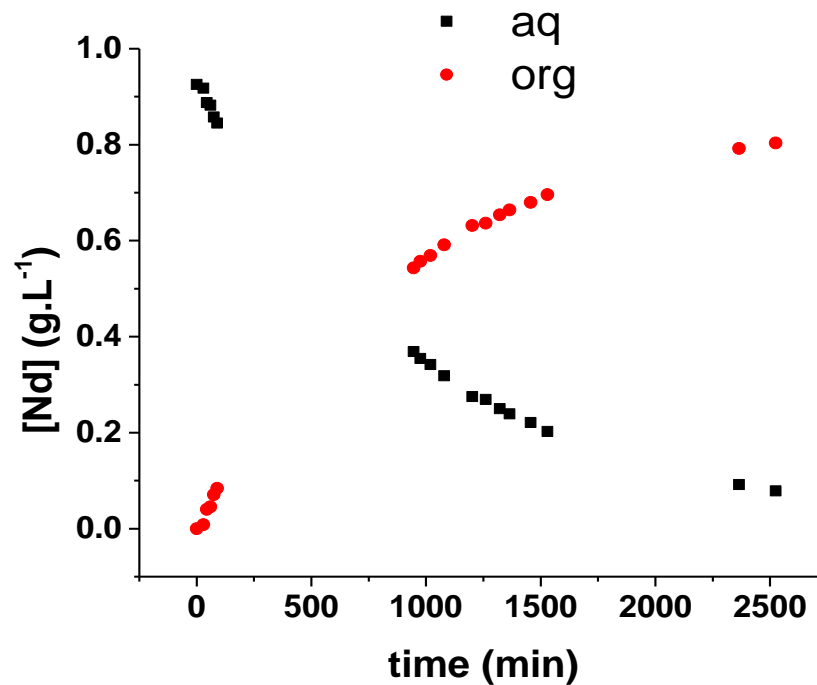
V_{pe} : volume of each aliquot (mL) ;

X : concentration of Nd ions in aqueous phase (g.L⁻¹), inlet (e) and n for the others aliquots

Y : concentration of Nd ions in solvent L phase (g.L⁻¹), inlet (e) and n for the others aliquots

Pertraction : experimental results

Nd concentration profile in aqueous and organic phases versus time :



Equilibrium is reached after 2500 minutes (42h)
with K_D (Nd) = $16,1 \pm 0,1$

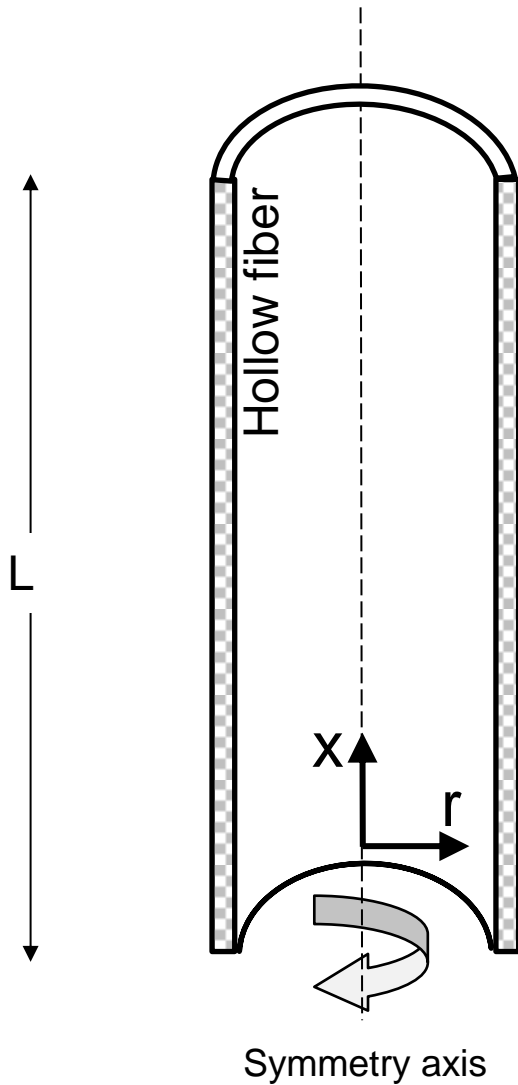
Pertraction : mass transfer simulation

Continuity equation:

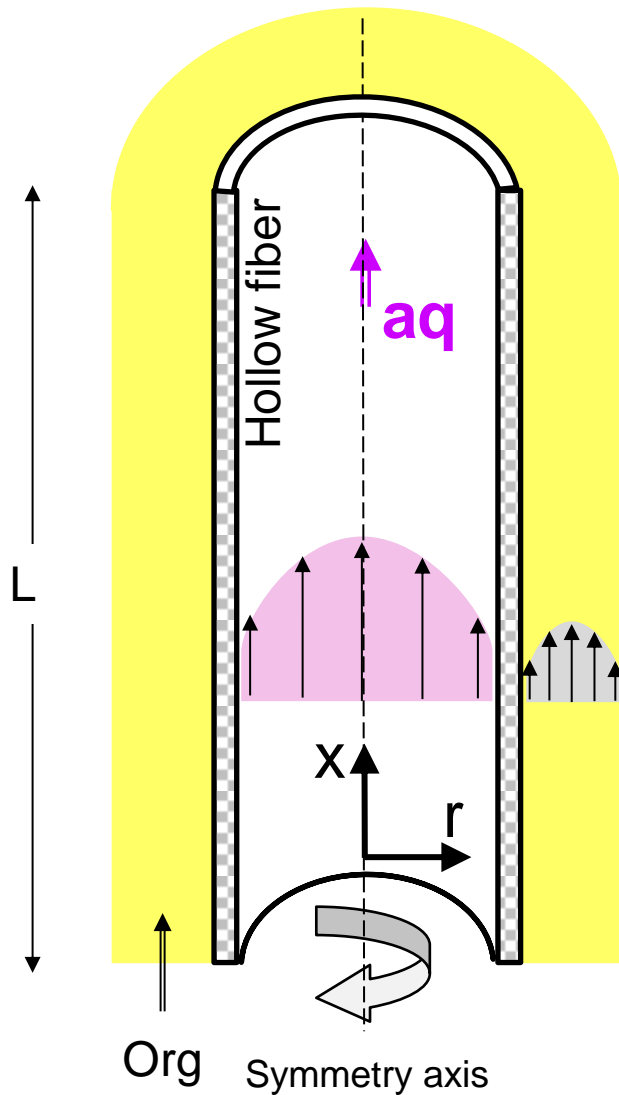
$$\frac{\partial C_i}{\partial t} + \nabla \cdot (-D_i \nabla C_i + C_i V_i) = 0$$

Assumptions :

Uniform pore size and fiber porosity throughout the fiber length



Pertraction : mass transfer simulation



Continuity equation:

$$\frac{\partial C_i}{\partial t} + \nabla \cdot (-D_i \nabla C_i + C_i V_i) = 0$$

Assumptions :

Uniform pore size and fiber porosity throughout the fiber length
Laminar flow with parabolic velocity profile in two phases in the contactor

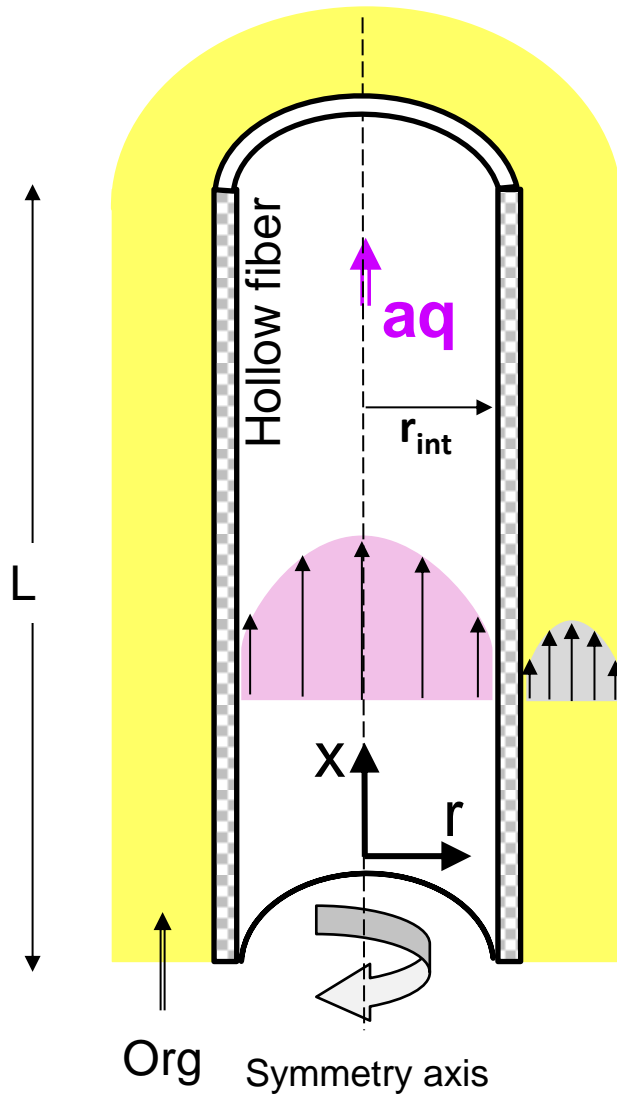
Solute is transported by diffusion and convection in the two phases :

$$\frac{\partial C_i}{\partial t} + \nabla \cdot (-D_i \nabla C_i + C_i V_i) = 0$$

Diffusion is the only transport mechanism in the membrane :

$$\frac{\partial C_i}{\partial t} + \nabla \cdot (-D_i \nabla C_i) = 0$$

Pertraction : mass transfer simulation



Complexing reaction occurs at the interface aqueous-membrane

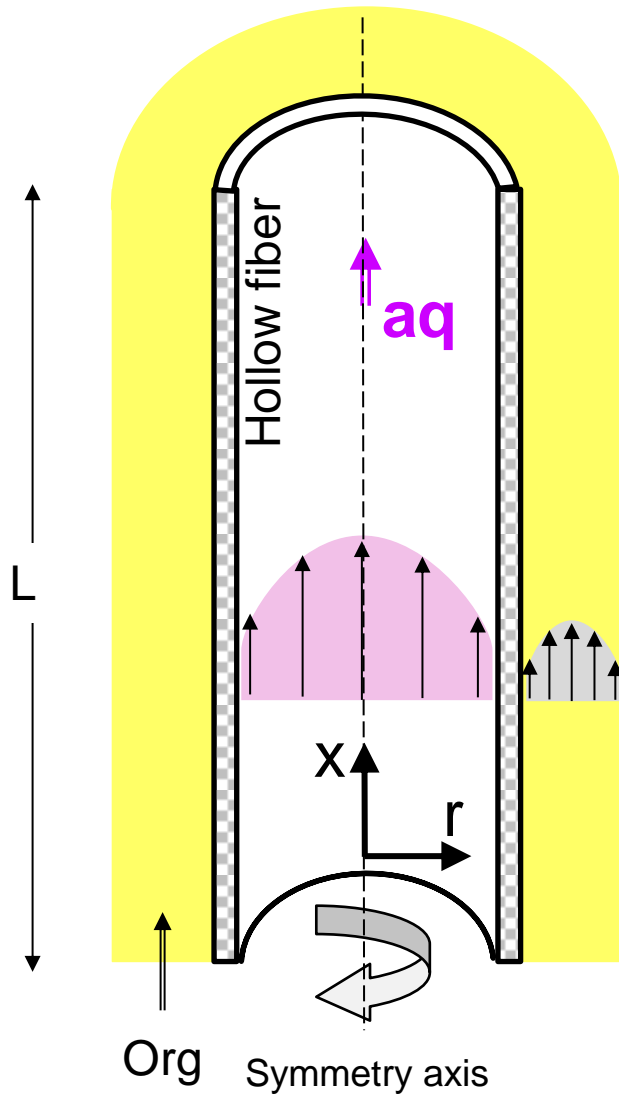


This chemical reaction is defined by a kinetic with flux expression :

$$\varphi \text{ (mol.m}^{-2}\text{.s}^{-1}\text{)} = k_v \cdot \left([\text{Nd}^{3+}]_{\text{aq}} - \left(\frac{[\text{NdL}_3(\text{NO}_3)_3]}{K_{\text{ex}} \cdot [\text{NO}_3^-]^3 \cdot [\text{L}]^3} \right) \right) = \frac{\partial [\text{Nd}^{3+}]_{\text{aq}}}{\partial r} \Big|_{r=r_{\text{int}}}$$

The model is solved by scilab 5.5.1 and is just optimised by one parameter k_v (m.s⁻¹) for best fitting experimental results.

Pertraction : mass transfer simulation



Simulation and prediction of Nd concentration in aqueous and solvent L phases

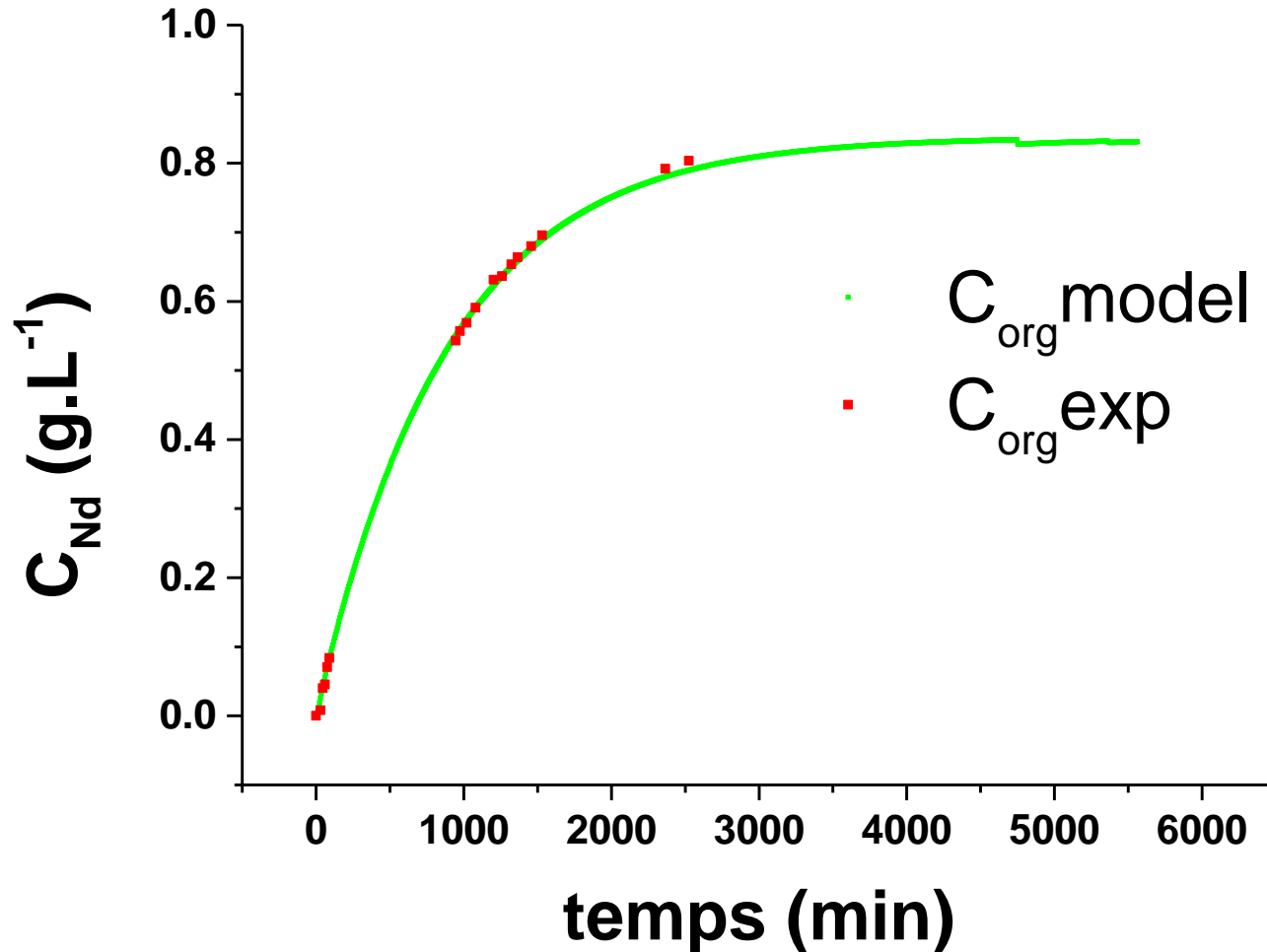
Input parameters

Geometric characteristics		Process variables	
R_{int}	$0.9 \cdot 10^{-3} \text{ m}$	K_{ex}	9.3210^{-3}
R_{intp}	$2.5 \cdot 10^{-3} \text{ m}$	D_{aq}	$6.16 \cdot 10^{-10} \text{ m}^2 \cdot \text{s}^{-1}$
e	$0.4 \cdot 10^{-3} \text{ m}$	D_{org}	$1.29 \cdot 10^{-10} \text{ m}^2 \cdot \text{s}^{-1}$
L	0.25 m	A	$40 \text{ mL} \cdot \text{h}^{-1}$
ε	80	O	$40 \text{ mL} \cdot \text{h}^{-1}$
τ	2	[solvent]	-

Neodymium's diffusion coefficient in solvent L and aqueous phases is determined experimentally by TDA

Pertraction : mass transfer simulation

Results



Simulation results were in good agreement with the experimental data for a value of $k_v = 5.10^{-7} \text{ m}\cdot\text{s}^{-1}$ which validated the model assumptions. This value of k_v is maintained for predict the influence of geometric characteristics and process variables.

General conclusion

Possibility to use solvent L to selectively extract REE and separate them each other from magnets waste in nitric media ;

Neodymium's extraction mechanism :



Exothermic reaction with $\Delta H_{\text{ext}}^0 = - 22.9 \text{ kJ.mol}^{-1}$

Taylor Dispersion analysis for determine Nd diffusion coefficient in aqueous and organic phases with $\text{RSD} \leq 3\%$: simple method fast and few sample volume needed (0,7 nL) ;

Installation and implementation of pertraction module for Nd extraction with hydrophobic polypropylene membrane which has low interfacial volumic area $230 \text{ m}^2.\text{m}^{-3}$;

Mass transfer simulation results were in good agreement with the experimental data for a value of $k_v = 5.10^{-7} \text{ m.s}^{-1}$ which validated the model assumptions. The value of optimise k_v is maintained for predict the influence of geometric characteristics and process variables.

Experimental determination of k_v by Rotative Membrane Cell (RSD) method

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